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^{11}B Nuclear Magnetic Resonance Study of Calcium-hexaborides

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Abstract: We have performed ^{11}B nuclear magnetic resonance (NMR) measurements to microscopically investigate an electronic structure of the ferromagnetic state in three different compositions of calcium-hexaboride single crystals. Although the crystal structure of CaB_6 is cubic and three NMR lines may be expected for the nuclear spin 3/2 of ^{11}B, a larger number of NMR resonance peaks have been observed. The frequency and intensity of those peaks distinctively changes depending on the angle between crystalline axis and magnetic field. Analyzing this behavior, we find that the electric field gradient(EFG) tensor at the boron has its principal axis perpendicular to the six cubic faces with a quadrupole resonance frequency $\nu_Q \approx 600$ kHz. Even though the magnetization data highlight the ferromagnetic hysteresis, ^{11}B NMR linewidth data show no clear microscopic evidence of the ferromagnetic state in three different compositions of CaB_6 single crystals.

INTRODUCTION

Recent discovery of the ferromagnetic state in CaB_6 systems ignites a great deal of research activity. Surprisingly, the ferromagnetic transition temperature exceeds 900 K without partially filled *d*- or *f*-shells. However, the ordered moment is exceedingly small. Thus CaB_6 doped by a small amount of La has been extensively studied to understand the high Curie temperature and the origin of weak ferromagnetism.[1,2] Among several scenarios,

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two scenarios draw attention; the excitonic insulator model and the low-density electron-gas model.[3, 4] These models are invoked in order to explain the high Curie temperature. Another possible illustration is the effect of defects or ferromagnetic impurities.[5, 6] Appearance of this illustration originates from abnormalities in its magnetic properties. The small ordered moment supports the third illustration. However, the narrow range of its dopant concentration stabilizing the ferromagnetism does not appear to be compatible.

Thus we have to reconcile this puzzling observation of the very high Curie temperature but the extremely weak ordered moment as well as the sharp dependence of the ferromagnetism on the doping concentration. Also, the challenging fact is that the ferromagnetic state is triggered without *d*- or *f*- orbitals.

Macroscopic probes such as SQUID (superconducting quantum interference devices), transport measurements and ARPES (angle resolved photo-emission spectroscopy), have made their efforts in investigating the ferromagnetic state. However, microscopic measurements such as NMR have not yet been extensively carried out. It is not clear whether the ferromagnetism is distributed over bulk or localized in surface or in impurity states. Even further, no microscopic evidence supporting the existence of ferromagnetic state is established. Therefore, microscopic probes are expected to play an important role in unveiling this intricate phenomenon. NMR spectroscopy is a powerful tool for the study of local electronic structure in condensed matters. Since the nuclear spin moment is a few orders of magnitude smaller than the electronic moment, a small change in the electronic magnetization is going to generate a dramatic change in the nuclear response to the local field.

In this paper, we report ^{11}B nuclear magnetic resonance (NMR) measurements for six samples of CaB_6 single crystals; $Ca_{0.99}B_6$, $Ca_{0.995}La_{0.005}B_6$ and $Ca_{0.99}La_{0.01}B_6$ using two different purities of boron.

EXPERIMENTS

CaB6 single crystals are synthesized using the high-temperature flux method. Three compositions of $Ca_{0.99}B_6$, $Ca_{0.995}La_{0.005}B_6$ and $Ca_{0.99}La_{0.01}B_6$ using the nominal purity of 99.9% (*3NB*) and 99.9999% (*6NB*) boron respectively are prepared to obtain 6 different

CaB_6 single crystals. Those single crystals of a few milligram with a needle shape were loaded into a home-made Teflon tube for NMR measurements. ^{11}B NMR measurements were carried at 4.5 K and room temperature at 4.7 T using our home-made pulsed spectrometers with a quadrature detection scheme. The phase-alternating pulse sequences were employed to significantly reduce the electromechanical vibration (ring-down) after pulses.[7] Since the spectrum is broad due to the quadrupolar broadening, the pulse width should be as short as possible for whole excitation of the entire spectrum. In this case, ~1μs pulse was utilized. The broad spectra were scanned by the Fourier transform of echo signals with different carrier frequencies.

RESULTS AND DISCUSSION

The structure of CaB_6 is cubic with a lattice constant of 4.145 Å. Six boron atoms form an octahedron in a cube made of six calcium atoms as shown in Fig.1. The ferromagnetic moment at 2 K of three samples using *3NB* is shown in Fig.2 These values are converted to 0.02 μ_B/La and 0.17 μ_B/La, respectively, for $Ca_{0.995}La_{0.005}B_6$ and $Ca_{0.99}La_{0.01}B_6$. These are extremely small magnitudes of ordered moments.

The gyromagnetic ratio of ^{11}B nucleus is $^{11}\gamma$ = 13.65979 MHz/T and thus the resonant frequency of the central transition at Ho = 4.7 T should be about ν_o = 64.2 MHz. This is the unshifted position of ^{11}B at 4.7 T and the reference of the shift (0% of shift). Since the crystal structure of CaB_6 is cubic and all six boron sites are equivalent, three NMR peaks are expected due to the quadrupolar broadening for the nuclear spin 3/2 of ^{11}B. However, a larger number of NMR resonance peaks have been observed depending on the angle between the crystalline axis and the magnetic field. In Fig.3(a) we display the ^{11}B NMR spectra with respect to the measured angle, Θ, between the crystal axis and the magnetic field. The alignment has been performed using a marking line for rotation of the sample container. From 3 up to 7 transition lines appear. The frequency and intensity of those peaks distinctively change depending on the measured angle Θ.

This spectrum is due to the structural symmetry of hexaborides. Since six boron ions constitute an octahedron at the body-center in the cubic cell of calcium ions in Fig.1, all

boron sites are equivalent. Also, the extension of the diagonal lines in the octahedron pierces a face center of the cubic cell. Consequently, one extension of the diagonal line in the boron

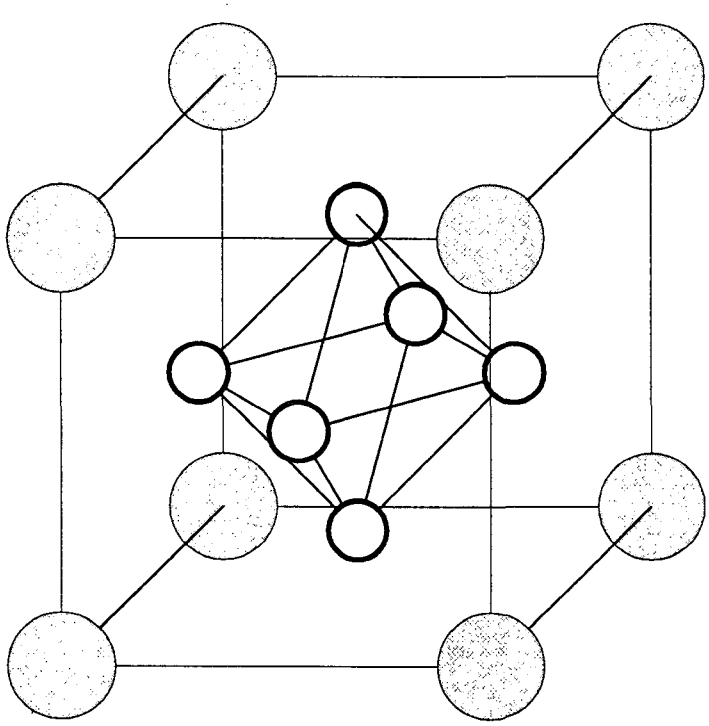

Fig. 1: The crystal structure of CaB_6. The lattice constant is 4.145 °*A*.

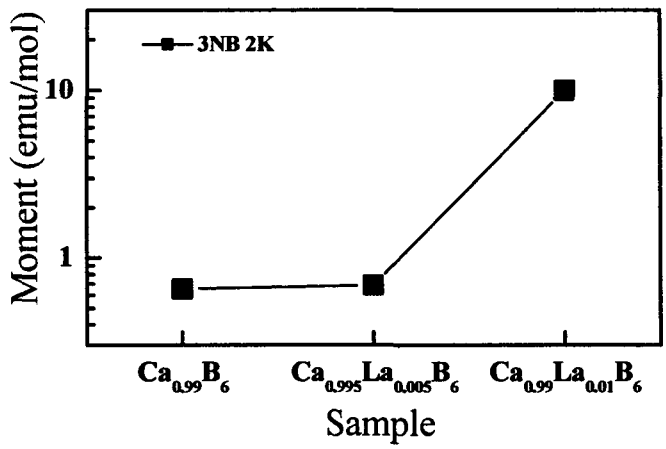

Fig. 2: The ferromagnetic moment at 2K for three samples using *3NB*.

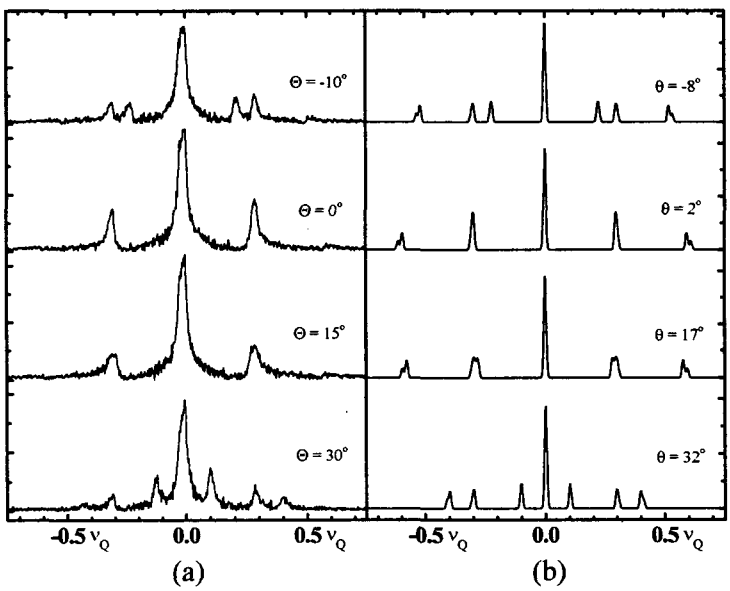

Fig. 3: ^{11}B NMR spectra of CaB_6 single crystal at 4.7 T and room temperature. The measured spectra are shown in (a) as a function of the measured angle Θ between the magnetic field and the crystal axis. The calculated spectra are shown in (b) as a function of the exact angle θ.

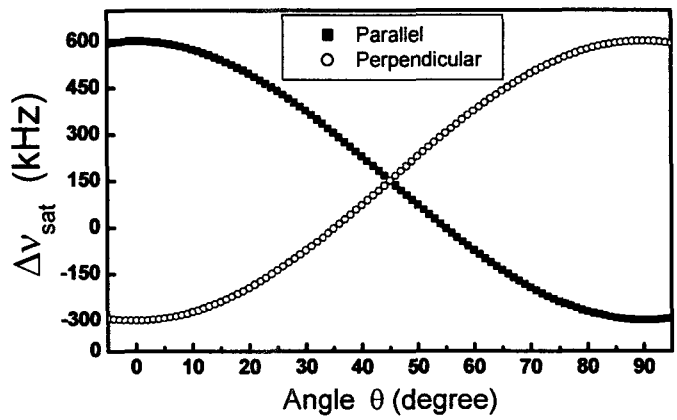

Fig. 4: The resonant frequency variation of the quadrupolar satellites, $\Delta\nu_{sat}$, as a function of the angle θ between H_O and the crystal axis.

octahedron is parallel to the crystal axis and the rest two extensions are perpendicular to the crystal axis.

Since all boron sites have an uniaxial symmetry, the principal axis of the EFG tensor at a specific boron site is the body diagonal of the boron octahedron crossing the very boron. Also, the asymmetry factor is $\eta \approx 0$. As a result, if an external magnetic field *Ho* is parallel to the crystalline axis (the *exact* angle $\theta = 0°$), then two borons have the principal axis (we denote it by the *c-axis*) of the EFG tensor parallel to *Ho* ($\theta = 0°$) and 4 borons have the c-axis perpendicular to *Ho* ($\theta = 90°$). Therefore, the spectrum for *Ho* parallel to the crystalline

axis show the two sets of three resonance lines; one central and two satellites. Taking the quantum mechanical transition matrix into account, we find that the resonance positions are $0, \pm 0.5\nu_Q, \pm\nu_Q$ from the unshifted position ν_o with the relative intensity of 4: 2: 1, where ν_Q is the quadrupole resonance frequency. For other directions of *Ho*, the spectrum will show various patterns. Analyzing this behavior, we indeed find the electric field gradient (EFG) tensor at the boron has the *c-axis* perpendicular to the 6 cubic faces with $\nu_Q \approx 600$ kHz.

Fig.3(b) shows calculated spectra based on these parameters. The simulated spectra exactly match the measured spectra for all different measured angles of rotation. This agreement confirms that the spectral analysis is correct, namely, the principle axis of the EFG tensor is perpendicular to the faces of the conventional cubic cell and $\nu_Q \approx 600$ kHz with $\eta \approx 0$. In addition, we find the measured angle Θ in Fig.3(a) differs by 2° from the exact angle θ in Fig.3(b) and the alignment of the crystal is correct within 2°.

Fig.4 shows the resonant frequency variation of the quadrupolar satellites as a function of the angle θ between *Ho* and the crystal axis, which is parallel to the *c-axis*.

$$\Delta \nu_{sat} = 0.5\nu_Q (3\cos^2\theta - 1).$$

Fig.5 shows the same variation for the central transition.

$\Delta \nu_{cent} = (3/16)(\nu_Q / \nu_o)(1-3\cos^2\theta)(9\cos^2\theta - 1)$. This variation for the central transition broadens the total central lines since the central transitions from the 6 borons are all added. The data in Fig.4 and Fig.5 consistently explain the distinctive variation of all ^{11}B NMR peaks shown in Fig.3(a). On the other hand, from $\Delta \nu_{sat}$ and $\Delta \nu_{cent}$, we find that $\pm\theta$ degree

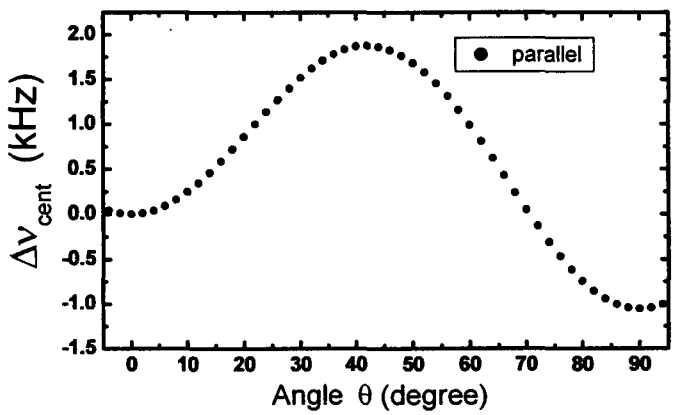

Fig. 5: The resonant frequency variation of the central transition, $\Delta \nu_{cent}$, as a function of the angle θ between H_O and the crystal axis.

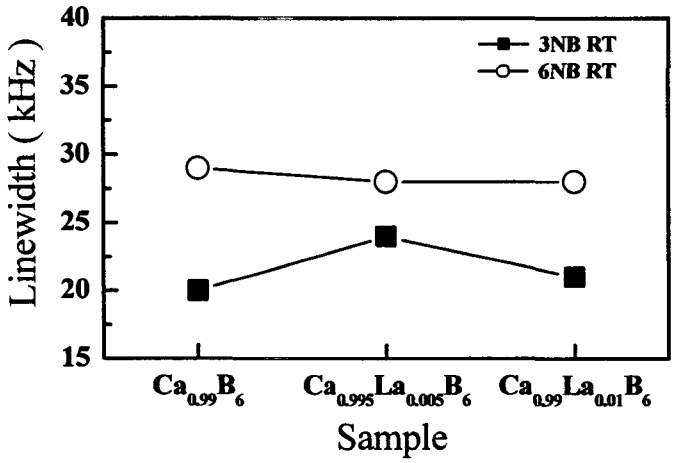

Fig. 6: ^{11}B NMR linewidth (FWHM; the full width at half maximum) of the central transition for six different samples. All three compositions using *3NB* show the ferromagnetic hysteresis. The ferromagnetic moment increases along the horizontal axis.

shift the NMR peaks equally. Then, it should be noticed that a small difference of 6° for -8° and 2° generates much different spectra in Fig.3(b).

Fig.6 shows the linewidth (FWHM; the full width at half maximum) of the central transition for ^{11}B NMR of CaB_6. The linewidth is smaller for three ferromagnetic samples made of *3NB*. Since ferromagnetism generates large local magnetic fields, the linewidth should dramatically increase. Thus this behavior is not compatible with the ferromagnetism. Therefore, all NMR data provide no microscopic evidence supporting the ferromagnetic moment.

No change of the shift and the smaller linewidth for the ferromagnetic crystals are inconsistent with the ferromagnetic signal observed from the magnetization hysteresis. However, this conclusion is based on a local moment picture affecting NMR shifts and linewidths. Namely, if a new scenario for the formation and distribution of ferromagnetic moment is devised, then NMR data may be influenced in a different way from this conventional picture. More microscopic measurements should be carried out to unveil the nature of this intriguing ferromagnetism.

CONCLUSION

We have performed ^{11}B NMR measurements at 4.7 T in order to find microscopic evidence and to investigate the nature of the ferromagnetic state in CaB_6. Although 3 NMR lines are expected for the nuclear spin 3/2 of ^{11}B, since the crystal structure of CaB_6 is cubic and so all boron sites are equivalent, a larger number of NMR resonances have been observed depending on the angle between magnetic field and the crystal axis. The frequency and intensity of those peaks distinctively change.

Analyzing this behavior, we find the electric field gradient(EFG) tensor at the boron has its principal axis perpendicular to the 6 cubic faces with the asymmetry factor of EFG tensor $\eta \approx 0$. and the quadrupole resonance frequency $\nu_Q \approx 600$ kHz. Using these parameters, we are able to simulate various NMR spectra consistent with the measurements as a function of angle between the crystal axis and magnetic field.

^{11}B NMR linewidth has been measured for six different single crystals of three compositions, CaB_6, $Ca_{0.995}La_{0.005}B_6$ and $Ca_{0.99}La_{0.01}B_6$, using *3NB* and *6NB* respectively. Even though the magnetization data clearly highlight the ferromagnetic hysteresis for three compositions using *3NB*, the ^{11}B NMR linewidths for the ferromagnetic crystals are smaller. Thus all ^{11}B NMR data are inconsistent with the ferromagnetism and show no clear microscopic evidence of the ferromagnetic state in CaB_6.

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